

Remarks:

This amendment is submitted in an earnest effort to advance this case to issue without delay. The examiner has indicated that the case contains allowable subject matter.

The specification has been amended to eliminate some minor obvious errors. No new matter whatsoever has been added.

The claims have been amended by combining the features of original claims 1, 2, and 3 into new US-style claim 15, canceling claims 1, 2, and 3, and heavily amending the other claims so they better comply with US practice. In addition new main claim 15 recites the spacing H3 between input line 1 and the base of the heat exchanger E as originally disclosed in paragraph [0012] of the present description. Further, we have integrated the dimensions H1, H2, and H3 into claim 1 according to FIG. 2.

The method feature concerning the utilization of the thermosiphon effect of original claim 9 is recited in amended claim 6.

US 4,822,393 of Markbreiter describes the pre-treatment of natural gas for reduction of the carbon dioxide content. The cooled gas leaves the exchanger 14 through line 18 and flows via lines 19, 20 into the bottom of absorption column or scrubber 21.

Therein, the gas is contacted with cold methanol for CO_2 absorption. Methanol with absorbed CO_2 is withdrawn from column 21 by line 24 and flows via lines 25 and 26 to a pressure reducing valve 27, discharging therefrom into flashing separator 28. Methanol drained from separator 28 passes via line 30 through heat exchanger 31 and the warmed methanol undergoes a second flashing separation in separator 32. Released CO_2 vapor exits through line 33 while liquid methanol flows through line 34 into heat exchanger 16. The methanol is warmed in exchanger 16 so that the methanol leaving through line 35 undergoes the third flashing separation in separator 36. Methanol draining through line 38 into pump 39 is raised to a pressure of 107 psis for recycling to scrubber 21. From pump 39 the methanol flows through line 40 and heat exchanger 31 to an external refrigeration exchanger 43 via line 44 into the scrubber 21. The method and device of Markbreiter may be recognized as the closest prior art to the subject matter of the present application.

Nonetheless new claim 15 has at least the following four additional features associated with specific advantages in comparison to the method and device according to Markbreiter:

1. According to the present invention, the methanol is not directly conducted from the liquid/ gas separator D into the absorber 5, but a generator 6 is arranged downstream the liquid gas separator D and, by further increasing the temperature and influx

of heated inert gas, the remaining carbon dioxide is desorbed from the methanol, before being redirected to the absorber 5.

2. In contrast to the system described by Markbreiter no pressure-reducing valve 27 is necessary, because the first pressure reduction from 55 bar from the absorber 5 to 9 bar takes place directly within the first expansion vessel A.

3. While according to Markbreiter, every separator 28, 32, and 36 is associated with a respective heat exchanger 53, 31, and 16, only one heat exchanger E is necessary for the present system. Consequently, the system according to claim 15 is much more compact, energy-efficient, and can be made at lower cost.

4. US 4,822,393 also of Markbreiter does further not disclose any specific dimensions regarding the arrangement of the plant features. But according to paragraph [0012] of the present description for effective implementation of the process of the invention it is of great importance that the vessels C and D and the heat exchanger E are arranged at a carefully determined height relative to each other. This ensures that the liquid flows in the intended direction through the heat exchanger E, without a pump being necessary. Consequently, liquid flow known as the thermosiphon effect develops automatically as a result of gravity and the condensing carbon dioxide. This can only be achieved with an arrangement according to the amended claim 1:

- The liquid level in the expansion vessel C is with a spacing of about 1 to 20 m (H1) above the liquid level in the liquid/gas separator D,
- The liquid level in the liquid/gas separator D is spaced about 0.5 m (H2) above the top side where heated methanol is vented from the heat exchanger E, and
- The spacing (H3) between the inlet line (1) for feeding methanol from the expansion vessel C into the bottom side of the heat exchanger E, and the base of the heat exchanger E is about 0.5 m.

Thus, it is particularly advantageous to exploit the targeted benefit of the thermosiphon effect in order to automatically establish liquid flow through the various components of the system unit in accordance with claim 1.

Even though a carbon dioxide/methanol separator downstream from separation vessels has been disclosed by Ranke in DE 390 2276 A1 and further separation systems for separating carbon dioxide from methanol are known from other documents cited in the Office Action, the specific arrangement of the reaction vessels and the heat exchanger E according to the amended claim 1 in order to make targeted use of the thermosiphon effect has not been disclosed by any of these documents.

Thus it is clear that the subject matter of the present application has not been anticipated by the disclosure of any documents cited by the Examiner to form a valid rejection under

§103. Further, the skilled person confronted with the object of providing an effective, reliable and cost effective process for removal of carbon dioxide from synthesis gases, has no indication on how to design the device and method according to the amended claim 1 in view of the cited prior art within the Office Action.

For these reasons the claims in the case are all clearly allowable. Notice to that effect is earnestly solicited.

If only minor problems that could be corrected by means of a telephone conference stand in the way of allowance of this case, the examiner is invited to call the undersigned to make the necessary corrections.

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SYSTEM ~~[[UNIT]]~~ FOR DESORBING CARBON DIOXIDE FROM METHANOL

CROSS REFERENCE TO RELATED APPLICATIONS

This application is the US national phase of PCT application PCT/EP2003/004112, filed 19 April 2003, published 15 January 2004 as WO 2004/004870, and claiming the priority of German patent application 10229750.9 itself filed 3 July 2002, whose entire disclosures are herewith incorporated by reference.

FIELD OF THE INVENTION

~~The object of the invention ~~[[is]]~~ relates to a system unit, which in for the total purification of compressed gases, and that makes it possible to recover methanol in a pure state ~~[[and]]~~ while at the same time utilize utilizing the ~~[[cold]]~~ thermal energy liberated in an extremely effective way.~~

BACKGROUND OF THE INVENTION

It is known that cold methanol has the capability of absorbing large amounts of gas impurities. Use is made of this capability in the Rectisol® process, in which the total purification of compressed gases is possible in a single process operation. The absorptive capability of methanol increases considerably at lower temperatures. At -60°C for example 75 times more carbon dioxide dissolves in methanol than in the same volume of water at 25°C, that is the methanol cycle amounts to 1/75 compared with water recirculation in a pressurized water cycle. At lower temperature the vapor pressure of methanol is so low that there is little use of solvent.

The Rectisol® process is particularly efficient when large amounts of gas impurities must be removed, or if a particularly high gas purity is required, and overall where the process can be built into the cold stage of a low temperature gas decomposition. In the latter case the process itself offers important advantages when only small quantities of gaseous impurities are to be washed out.

Gas washing is carried out such that the standing raw gas is treated with methanol under medium pressure of 5 to 40 atmospheres or also under high pressure of 50 to 200 atmospheres at temperatures between 10°C and -80°C.

~~Thereby~~ This way, all gaseous impurities such as raw gasoline, crude benzene, ammonia, hydrocyanic acid, resin formers, organic sulfur and phosphorus compounds, carbonic acid, hydrogen sulfide, iron and other metal carbonyls and water are absorbed. The loaded-up methanol is then regenerated by expansion, evaporation, or heating, and subsequently re-used. The impurities can be recovered from the off-gases or condensate. This process is the subject of German patent 1 544 080 (US 3,453,835).

An especially important gas purification process known ~~[[to]]~~ in the art includes purification of, for example, synthesis gases ~~[[,]]~~ produced from natural gas gasification processes, which are the starting point for a variety of major technical syntheses. Raw synthesis gas contains considerable amounts of carbon dioxide ~~[[the]]~~ whose removal ~~of which~~ is

crucially important for the further use of synthesis gasses. The development of effective, reliable, and cost-effective processes for removal of carbon dioxide from synthesis gasses is therefore of considerable importance for the efficient winning production of a variety of applicable gas mixtures.

It has now been found that the process known up until now for the purification of gases with methanol may still be improved considerably, if the system [[unit]] in accordance with the invention, and the process that may be carried out therein for desorption of carbon dioxide, is employed.

OBJECT AND SUMMARY OF THE INVENTION

The object of the invention is therefore a system [[unit]] for desorption of carbon dioxide and other impurities from methanol held under high pressure, comprising one or a plurality of expansion vessels arranged in sequence, at least one heat exchanger and at least one liquid/gas separator, in which

(a) A line (1) is provided through which the strongly cooled methanol leaving the expansion vessel C is introduced from below into the heat exchanger and

(b) a line (2) is provided, through which the heated methanol above is transported from the top of the heat exchanger E, and is connected to a liquid/gas separator, in which the remaining carbon dioxide contained in the methanol is desorbed and separated to the greatest extent possible.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 shows an entire installation for desorption of carbon dioxide and other impurities from methanol held at high pressure, while

Figure 2 depicts the system ~~[[unit]]~~ in accordance with the invention and discloses further technical details ~~thereby~~.

SPECIFIC DESCRIPTION

For effective implementation of the process in accordance with the invention it is of great importance that ~~[[the]]~~ three reaction vessels C, D and E be arranged at a carefully determined height relative to each other. ~~[[That]]~~ This allows one in fact to ensure that the liquid flows in the wanted direction through ~~[[the]]~~ a heat exchanger E, without a pump being necessary. Liquid flow known as the thermo-siphon effect develops automatically as a result of gravity and the condensing carbon dioxide. ~~[[That]]~~ This can only be achieved ~~though~~ in the system ~~[[unit]]~~ in accordance with the invention in which:

(a) the liquid level in the downstream expansion vessel C is located about 1 to 20 m above the liquid level in the liquid-gas separator;

(b) this again is located about 0.5 m above the top-side ~~[[of]]~~ discharge opening for the heated methanol provided in the heat exchanger E;

(c) the distance between the inlet line ~~[[() 1 ()]]~~, from the bottom side of the heat exchanger E, for the methanol

fed from the expansion vessel C, and the base of the heat exchanger E is about 0.5 m.

Self-evidently the system [[unit]] in accordance with the invention can be operated by use of pumps, however it is particularly advantageous to exploit application of the thermo-siphon effect so to automatically establish liquid flow through the various components of the system [[unit]] in accordance with the invention.

The system [[unit]] in accordance with the invention is downstream [[to]] from an absorber [[(]] 5 [(]]], which is provided for purification of synthesis gas with methanol. In addition, in accordance with the invention a regenerator [[(]] 6 [(]]] is downstream [[to]] from the system [[unit]], in which, by further increasing the temperature and influx of a heated inert gas - such as for example methanol vapor - the remaining carbon dioxide is desorbed from the methanol,.

In the absorber [[(]] 5 [(]]] the raw gas flowing in from below through the counter-flowing cold methanol [[,]] is purified. The outgoing liquid from [[below]] the base of the absorber [[(]] 5 [(]]], containing all the impurities of the raw gas, is cooled in the heat exchanger E and fed into the expansion vessel [[(]] A [(]]]. The purified synthesis gas leaves at the top of the absorber.

In the upstream expansion vessel A the methanol held under a pressure of 55 atmospheres is expanded to about 9 atmospheres and at a temperature of -45°C desorbs mainly hydrogen

and carbon monoxide, which after passage through the heat exchanger E are obtained as gas fractions for the process. The liquid fraction from the expansion vessel A is then fed through a line to a second or middle expansion vessel B.

5 In the middle expansion vessel B the methanol pressure is lowered from about 9 atmospheres to about 2.7 atmospheres and thereby a temperature decrease from about -45°C to about -52°C is obtained. In this case gaseous carbon dioxide is released from the methanol, which is passed through the heat exchanger E and
10 may subsequently be credited to the process, while the liquid fraction obtained is fed to a third or downstream expansion vessel C.

In the downstream expansion vessel C the pressure of the methanol solution is decreased from about 2.7 atmospheres to
15 about 1.2 atmospheres and thereby a further temperature decrease from about -52°C to about -60°C is observed. Also in this downstream expansion vessel C, gaseous carbon dioxide is obtained, which likewise is fed to heat exchanger E and can subsequently be credited to the process.

20 The liquid fraction obtained in the downstream expansion vessel C is then preferably divided into two streams, wherein one stream being fed to the upstream absorber 5 and the second stream being fed through the line 1 to the heat exchanger E, which itself, for
25 the methanol heated there, is connected by line 2 with the liquid-gas separator D.

The liquid-gas separator D has a branch line ~~[[()]]~~ 3 ~~[[()]]~~ for gaseous carbon dioxide, as well as another line in which ~~[[the]]~~ liquid methanol 4 is taken from below the separator D and fed to the downstream regenerator ~~[[()]]~~ 6 ~~[[()]]~~. The

5 liquid fraction ~~[[()]]~~ 4 ~~[[()]]~~ taken from the liquid/gas separator is fed to the downstream regenerator ~~[[()]]~~ 6 ~~[[()]]~~ to remove the last traces of carbon dioxide, which are extracted by further increasing the temperature and feeding in a stream of heated gas, for example methanol vapor. ~~While the~~ As carbon dioxide is taken

10 from the process, the ultrapure methanol produced in the regenerator 6 is fed back to the absorber ~~[[()]]~~ 5 ~~[[()]]~~ and remains there to be available again for the purification of a fresh stream of raw gas.

Overall the process in accordance with the invention is

15 therefore characterized in that carbon dioxide is desorbed from methanol stepwise in a plurality of expansion vessels, at least one heat exchanger, and at least one liquid/gas separator. Here the methanol leaving the expansion vessel has a temperature of $-60 \pm 10^{\circ}\text{C}$ and a pressure of 1 to 2 atmospheres. The cold

20 ~~liberated~~ thermal energy recovered by the heat exchanger E represents a valuable energy source available for other cooling reactions. In this instance the temperature of the methanol stream increases in the heat exchanger to $-10 \pm 5^{\circ}\text{C}$, and the liquid stream is fed to the liquid/gas separator at this

25 temperature.

The process in accordance with the invention and the system [[unit]] associated with it thus make possible in an exceptionally purposeful manner the purification of enriched methanol, in the total removal of the contained pressurized gases and impurities, especially carbon dioxide. At the same time, the cold of vaporization resulting from desorption of carbon dioxide is recovered which is of great significance for absorption processing.

The material streams in the system [[unit]] in accordance with the invention show the indicated parameters in Table 1 below.

Material Stream	1	2	3	4
Stream Parameters				
Carbon Dioxide	11.45	11.45	98.10	1.44
Methanol	88.55	88.55	1.92	98.56
Temperature	-59.5	-8.8	-8.9	-8.9
Pressure (in absolute atm)	1.20	1.20	1.15	1.15
Vapor Proportion	0.00	0.10	1.00	0.00
Flow Velocity (t/h)	585	585	80	505